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van Veen, G.N.A.; van Veen, A.; Oostra, D.J.; de Vries, A.E.

Published in:
Physical Review Letters

DOI:
10.1103/PhysRevLett.57.739

Anomalous Time-of-Flight Distributions Observed for Argon Implanted in Silicon and Resputtered by Ar^+-Ion Bombardment

G. N. A. van Veen, F. H. M. Sanders, and J. Dieleman
Philips Research Laboratories, 5600 JA Eindhoven, The Netherlands

A. van Veen
Interuniversity Reactor Institute, Technische Hogeschool Delft, 2629 JB Delft, The Netherlands

and

D. J. Oostra and A. E. de Vries
Institute for Atomic and Molecular Physics, Foundation for Fundamental Research on Matter, 1009 DB Amsterdam, The Netherlands
(Received 27 December 1985)

A Si substrate is bombarded by 3-keV Ar^+ ions. From time-of-flight spectra of resputtered Ar neutrals at various target temperatures, we conclude that Ar-bubble formation takes place in the amorphized-Si top layer. The bubbles form and open during etching. The average kinetic energy of the Ar atoms is in agreement with the calculated average potential energy of the Ar atoms inside the bubbles.

PACS numbers: 61.80.Jh, 79.20.Nc

Noble-gas kiloelectronvolt ion bombardment of solids is known to cause (material removal by) sputtering, ion implantation, and changes in the structure of the surface layer. In nearly all cases the most abundant species sputtered from an elemental solid are atoms. The kinetic energies of most ejected target atoms obey a single collision-cascade (CC) like distribution of the form $dN/dE = CE/(E + U_0)^3$ where dN is the number of particles in the kinetic energy interval dE, C is a constant, and U_0 is the effective surface binding energy.[1] Values of U_0 vary widely. For example, for silicon $U_0 = 7.8$ eV,[2] whereas condensed noble-gas atoms have a $U_0 = 0.02$–0.03 eV.[3] A considerable part of the noble-gas ions impinging on the surface is implanted and accumulates in the solid. At room temperature and at fluences of 10^{14}–10^{17} ions/cm^2 these implanted noble-gas atoms have been reported to be present in metals as single atoms as well as small gas bubbles.[4,5] Recently it has been shown that the internal pressures in such bubbles can be sufficient for the gas to solidify.[6] It may be expected that in the case considered in this paper, viz., Ar in Si, bubble formation will also take place. However, data are scarce. Bean *et al.*[7] have observed Ar bubble formation in Si after annealing a sample which was kept at 800 K during 1-keV Ar^+ ion bombardment. Wittmaack[8] has observed an enhancement in the sputtering yield related to implantation of primary noble-gas ions in silicon. He suggests that the increased sputtering rate is due to the action of released gas atoms. Recent work by Feenstra and Oehrlein[9] gives some evidence for bubbles upon bombardment of Si with 700-eV Ar ions. They observe 50-Å-diameter hillock formation at the surface and attribute these hillocks to the initial stage of cone formation or to Ar clustering in the Si matrix. The sputtering of Si by Ar^+ ions has been studied extensively. Some work has been done by Kolfschoten *et al.*[10] on the resputtering of implanted Ar in Si but so far no detailed time-of-flight (TOF) experiments have been performed on the implanted and subsequently ejected argon atoms. This information sheds light on how implanted Ar atoms are situated in the silicon matrix.

In the present work a Si target at temperatures between 50 and 290 K is bombarded by 3-keV Ar^+ ions. The TOF distribution of resputtered Ar neutrals is measured under steady-state conditions. The experimental setup used in this work has been described in detail in previous papers.[3,11] Therefore only a brief outline of the apparatus will be given. A p-type Si $\langle 111 \rangle$ sample is mounted on the tip of a He cooling machine. The temperature of the tip can be varied from 20 K to room temperature by means of a resistance heating element. The substrate is bombarded by a beam of 3-keV Ar^+ ions with a flux of about 5×10^{14} ions/s cm^2, which comes in at 60° to the surface normal. After a flight path of 37 cm the Ar neutrals ejected from the surface along the surface normal are ionized, pulled into a quadrupole mass spectrometer, mass selected, and detected by a particle multiplier. The incident ion beam is chopped electrostatically with a pseudorandom code. After deconvolution the TOF of the sputtered particles is obtained.

The TOF distributions of Ar at target temperatures of 80, 100, and 290 K are displayed in Figs. 1(b)–1(d). Two distinct contributions can be seen, which can be

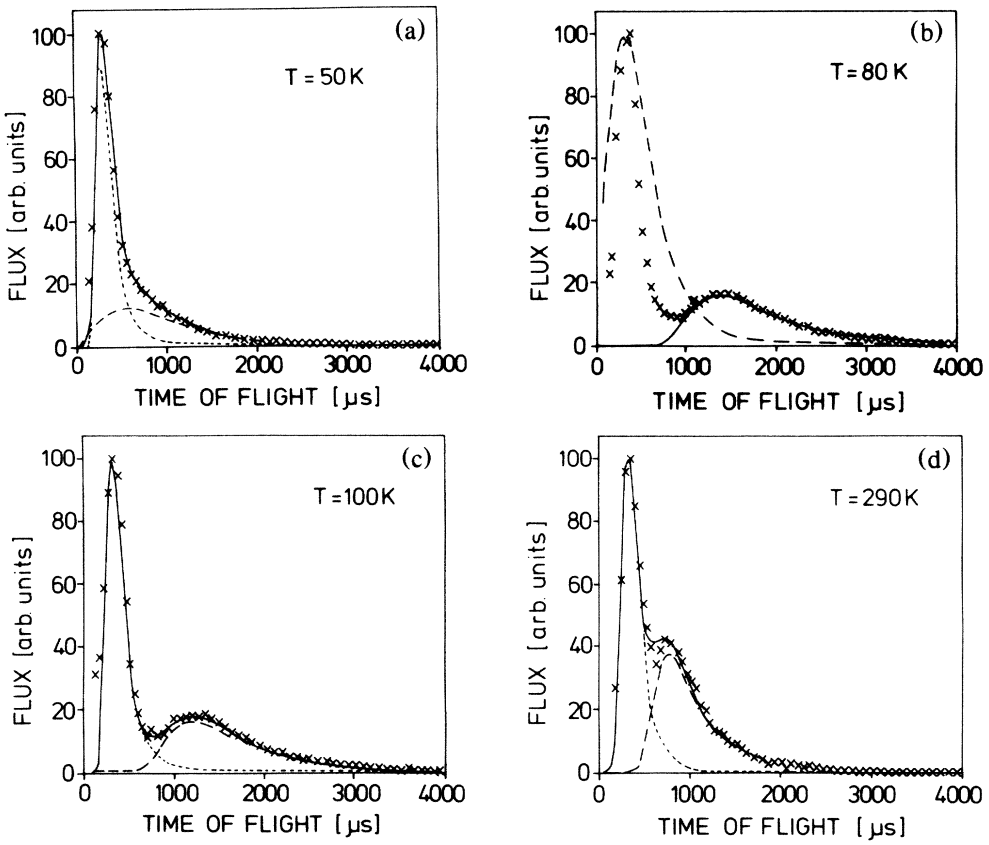

FIG. 1. Time-of-flight of Ar neutrals (flux distribution) from Si bombarded by 3-keV Ar^+ ions. (a) The total simulation of the spectrum is given by the solid line and consists of a MB distribution at 2000 K (short-dashed line) and a CC contribution with $U_0 = 0.02$ eV (long-dashed line). (b) The total simulation consists of MB distributions at 1650 K (not indicated) and 74 K (solid line). The dashed curve is a CC distribution with $U_0 = 0.075$ eV. (c) The total simulation (solid line) consists of MB distributions at 1650 K (short-dashed line) and 95 K (long-dashed line). (d) The total simulation (solid line) consists of MB distributions at 1850 K (short-dashed line) and 275 K (long-dashed line).

simulated by Maxwell-Boltzmann (MB) type distributions: one at target temperature and one at a much elevated temperature. The peaks at long flight time can be fitted with MB distributions at temperatures of 74, 95, and 275 K, respectively. These values are in good agreement with the temperature settings. The high-velocity peaks in Fig. 1 cannot be simulated with CC-type distributions. This is demonstrated in Fig. 1(b). A MB distribution at high T fits much better to the measured TOF distributions. In Figs. 1(c) and 1(d) examples for simulations of the total TOF spectra are given. Also the separate MB contributions at low (95 and 275 K) and high (1650 and 1850 K) temperatures are displayed. Generally the optimal simulations to the high-velocity peaks are obtained with MB distributions in which T ranges from 1650 to 2000 K, corresponding to average kinetic energies of 0.14 to 0.17 eV, respectively. For all spectra this peak contains about 60% of the signal. The experiment at 50 K [see Fig. 1(a)] is a special case because at this temperature the evaporation rate of Ar is very small.[12] Therefore no MB contribution at target temperature is observed. A second contribution must be present to account for the low-energy tail in this spectrum. The good fit shown in Fig. 1(a) is obtained for a combination of a CC distribution with an effective binding energy $U_0 = 0.02$ eV and a MB distribution with $T = 2000$ K. This value of U_0 is in good agreement with the values found by Haring *et al.*[3] in sputtering of noble gases. In the TOF spectrum about 40% of the signal is in the CC spectrum. This is close to the fraction of the signal found in the low-temperature MB distributions at other temperatures.

The anomalous doubly peaked TOF spectra might be explained by the presence of bubbles in the amorphized Si surface layer. Argon, at 3 keV energy, incoming at an angle of 60° to the normal, will penetrate the sample with an average depth of about 40 Å. The equilibrium Ar concentration in this layer upon bombardment with kiloelectronvolt ions will be about

1×10^{15} Ar/cm^2.[13] Even at concentrations of 1×10^{14} Ar/cm^2 clustering may take place. Implanted Ar can migrate because of ion-induced diffusion and the average distance between the Ar atoms and the surface is larger than the average Ar-Ar distance. Scherzer[5] indicates that at fluences between 10^{14} and 10^{17} ions/cm^2 (called intermediate fluences) formation of small bubbles takes place in metals upon bombardment with He. Also Bean's results[7] suggest this phenomenon. The experimental results in Fig. 1 can then be explained as follows. In the steady-state condition bubbles will be present and will be excavated because of the continuing etching. If the Si matrix cannot hold a bubble any longer it will expand explosively, giving rise to the high energy peaks in the TOF spectra. The MB distributions at target temperature > 50 K originate from ion-induced desorption (it must be remembered that only signal "in phase" with the chopped ion beam is detected), i.e., Ar from the implantation layer moves into the porous region below the surface[14] by ion-induced diffusion, thermalizes, and evaporates. Therefore no single Ar atoms will be present in the near-surface region for $T > 50$ K. At 50 K evaporation can no longer take place. Instead Ar atoms will be present on and near the surface resulting in a CC contribution in the spectrum.

The fact that the intensity ratio of the high-temperature and target-temperature MB peaks (for $T > 50$ K) is temperature independent is in agreement with this mechanism because ion-induced diffusion is a temperature-independent process.[15] It also explains why at temperatures as low as 50 K bubbles are still formed.

To investigate whether the observed average kinetic energies of 0.14–0.17 eV for the Ar atoms, in the high-energy peaks of the TOF spectra, could be characteristic of gas escaping from a bubble we performed calculations on spherical clusters of Ar atoms embedded in Si. These calculations are analogous to the ones performed by Finnis, van Veen, and Caspers.[16] The energy of the gas-filled cavities consists of three parts: the Ar-Ar and Ar-Si interaction energies and the elastic energy in the lattice from the strain induced by the bubble. The Ar-Ar interaction potential is of the Born-Mayer type $V(r) = A\exp(-br)$, where $A = 22$ keV and $b = 4.01$ Å^{-1}.[17] The shear modulus μ, the surface energy density γ, and the Burgers vector **b** are taken from crystalline Si data: $\mu = 6.8\times10^{10}$ N/m^2 and $\gamma = 1.69$ J/m^2 (Miedema[18]). Following observations made for He in metals,[4] we take small clusters with diameters between 12 and 23 Å containing 70 to 350 Ar atoms. The value of the average potential energy per Ar atom in the cluster (including the Ar-Si interactions and the stress induced in the Si lattice) varies from 0.1 to 0.7 eV.

The lowest values are obtained for the situation where the term including μ, the strain energy, is omitted. It should be noted that the experimental situation is somewhat different from the calculated ones: The clusters may not be spherical; the material will be amorphous, influencing the values of μ; and the cluster is near the surface, which will probably give rise to relaxation. The correct average potential energy per Ar atom may therefore be lower than obtained from our calculation. Nevertheless, the average kinetic energy found in the experiments is in the range of the potential energy predicted by the calculations. It is not yet clear to us whether the good fits of the high-energy peaks in the TOF spectra with MB distributions mean that we have to deal with a real temperature, and if so, how the potential energy of the Ar clusters is converted into kinetic energy. Further research is needed to clarify these points.

In conclusion, we have observed anomalous TOF distributions of Ar atoms ejected from Si upon bombardment by 3-keV Ar^+ ions. The doubly peaked spectra can be explained by Ar bubble formation, which occurs even at temperatures as low as 50 K. Ion-induced diffusion seems to be the mechanism determining the kinematics of the process. The average kinetic energy of the Ar atoms as determined in the experiment is in the range predicted by calculations.

This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (Foundation for Fundamental Research on Matter) and was made possible by financial support from the Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek (Netherlands Organization for the Advancement of Pure Research) and the Philips Research Laboratories.

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